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LETTER

Spontaneous Stoichiometry Change in Single Crystals of Superconducting $(Ba_{1-x}K_x)Fe_2As_2$ Grown by a Rapid-Heating Sn-Flux Method

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Abstract To prevent the loss of K in growing single crystals of $Ba_{1-x}K_xFe_2As_2$ we developed a rapid-heating Sn-flux method. Large single crystals with the optimal superconducting transition temperature $T_C \approx 38$ K were obtained and their structural, chemical and superconducting properties were investigated. Additionally, the effect of post-growth annealing on these crystals at different temperatures was examined. Scanning electron microscopy microprobe studies on a crystal with the composition goal of $Ba_{0.25}K_{0.75}Fe_2As_2$ revealed a well defined separation of two phases with compositions that are suggestive of rational ratios of the K and Ba content.

Keywords Iron arsenide superconductors · Crystal growth · Stoichiometry

The finding of high-T_C superconductivity up to 55 K in layered FeAs-based compounds and the observation of a spin-density wave transition (SDW) at ∼140 K [1–3] has stimulated broad research to investigate the nature of the superconducting phase and the role of the SDW for superconductivity in these systems. Electronic and magnetic properties reported so far, indicate some similarities between the properties of the FeAs-based systems and those of high-T_C oxocuprates. In order to study these relationships more deeply and to refine some of the published preliminary results, growth of large single crystals with well defined and reproducible stoichiometry is crucial. Similar to high-T_C oxocuprates the growth of homogeneous, and impurity free single crystals of the FeAs-based compounds was found to be difficult. So far, rather small single crystals of the layered oxopnictides $LnFeAs(O_{1-x}F_x)$ (Ln = Pr, Nd, Sm) were grown by using a NaCl/KCl flux method [4, 5]. Larger crystals of $AE_{1-x}K_xFe_2As_2$ (AE = Ba, Sr) were obtained by using either a Sn-flux or a self-flux method [6–9]. Although both methods provide single crystals with nominally the same structure and lattice parameters as those of powder samples, significant differences in the electronic and magnetic properties between single crystals and polycrystalline samples were observed.

At room temperature $BaFe_2As_2$ crystallizes with the well-known tetragonal $ThCr_2Si_2$ structure-type (space group $I4/mmm$) [3]. The crystal structure of $BaFe_2As_2$ can be described as alternate stacks along the tetragonal axis of Ba and Fe_2As_2 layers. At ∼140 K polycrystalline samples show a first-order phase transition to an orthorhombic structure (space group $Fmmm$) accompanied by a magnetic phase transition [3]. Partial substitution of Ba^{2+} by monovalent K or Cs induces superconductivity with T_C's as high as 38 K [3, 10, 11]. First studies of polycrystalline samples of $Ba_{1-x}K_xFe_2As_2$ as a function of x indicate that the nature of the magnetic transition can be described as a SDW which for $x \to 0$ appears at 148 K [3, 12]. As x increases, the transition temperature decreases and the SDW coexists with superconductivity below $x \approx 0.4$ for the $Ba_{1-x}K_xFe_2As_2$ system. The superconducting transition temperature T_C passes a maximum of ∼38 K for phases with $0.4 < x < 0.6$, and decreases to 3.8 K for pure KFe_2As_2. There have been several diverging reports on the magnetic and electronic properties of single crystals

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of $Ba_{1-x}K_xFe_2As_2$ [6, 13]. Crystals of $BaFe_2As_2$ grown by the self-flux method were rather small but showed a metallic resistivity down to 4 K with the structural and SDW transition between 130 K to 138 K [13]. However, significantly larger crystals obtained by the Sn-flux method showed a semiconductor behavior with a decrease of the structural and the SDW transition to ∼85 K. This observation has been attributed to inclusion of about 1% Sn into the $BaFe_2As_2$ crystals [6]. Nominal $Ba_{0.56}K_{0.44}Fe_2As_2$ single crystal with T_C's near ∼27 K showed a variation of the K concentration of up to 7% across the measured sample [6]. The comparatively low T_C of ∼27 K observed in these crystals has also been associated with the inclusion of ∼1% Sn.

In order to investigate these issues, especially why the rather large crystals grown by the Sn-flux technique exhibit electronic and magnetic properties significantly different from those of polycrystalline powders and crystals grown by the self-flux method, we systematically modified the Sn-flux method and examined the magnetic and electronic properties of crystals obtained by employing different growth conditions. We found that rapid initial heating provides single crystals with optimized magnetic and electronic properties. The influence of post-growth annealing on such crystals has also been studied.

To grow single crystals of $Ba_{1-x}K_xFe_2As_2$, FeAs was used which had been obtained by reacting stoichiometric amounts of high purity powder of Fe and As for 10 hours at 700 °C in an evacuated quartz glass tube. Subsequently, stoichiometric amounts of high purity Ba and FeAs, and twice the stoichiometric amount of K and Sn metal (molar ratio ≈1:50) were filled into ∼2 ml alumina crucible and sealed into a quartz ampoule under ∼0.4 bar of high purity Ar atmosphere. In order to avoid the loss of K and formation of unwanted K compounds below 700 °C the quartz glass ampoules were, in contrast to previously used procedures, placed directly in an oven which had been preheated to 700 °C. The oven was programmed to reach 850 °C within 2 hours and stay at this temperature for another hour followed by slow cooling to 500 °C within 36 hours. Finally, the ampoule was tipped from vertical to horizontal position at 500 °C, the oven was turned off and the sample was allowed to cool inside the oven. The quartz glass ampoule remained clear and showed no brownish dimming due to a reaction of the quartz glass with evaporated potassium.

A large number of $Ba_{1-x}K_xFe_2As_2$ crystals were obtained by this method. Large plate like single crystals of sizes up to $5 \times 5 \times 0.15$ mm^3 were easily separated from the Sn flux (see insert of Fig. 1). Several batches of single crystals of $Ba_{1-x}K_xFe_2As_2$ were grown aiming at compositions of $x = 0.45$ and $x = 0.75$.

The structural properties of the crystals were characterized using single crystal x-ray diffraction. The chemical composition was analyzed by microprobe analysis using

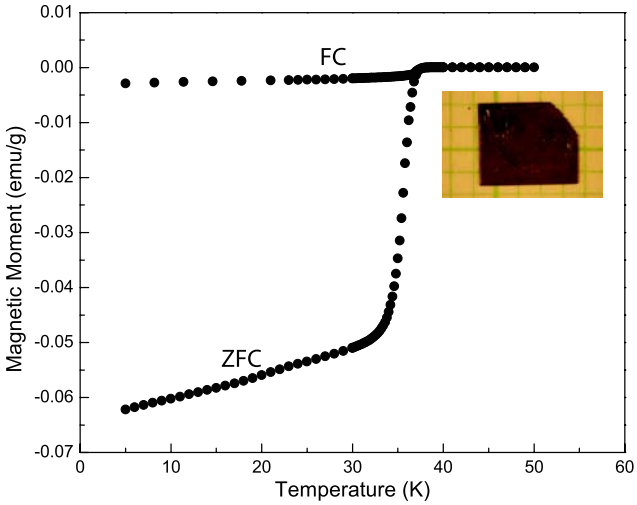

Fig. 1 (Color online) Temperature dependence of the magnetization of a $Ba_{65}K_{45}Fe_2As_2$ crystal determined in a magnetic field of 10 G aligned within the a–b plane measured in zero-field (ZFC) and field-cooled (FC) conditions. The *insert*: picture of the c-axis oriented crystal with a grid paper (mm-scale) given as a background

a Scanning Electron Microscope EOS TESCAN equipped with an Oxford EDX microprobe analyzing unit. The temperature dependence of the magnetization and the electrical resistivity was determined in a Quantum-Design magnetometer (MPMS) and a physical property measurement system (PPMS) (both systems from Quantum Design, 6325 Lusk Boulevard, San Diego, CA), respectively.

A first visual inspection of the crystals revealed traces of Sn on the surface of the crystals which can be removed mechanically or by cleaving off the upper layers of the crystal by an adhesive tape. The microprobe analysis of the samples confirmed traces of Sn (less than 1%) in some of the samples while the cleaved samples did not show any Sn within the accuracy of the EDX system.

Single crystal x-ray diffraction in transmission geometry of the large crystals with composition $Ba_{0.55}K_{0.45}Fe_2As_2$ (according to microprobe analysis) used for the measurements of the physical properties indicated perfect a–b planes (lattice parameter $a = 0.3930$ nm) but strong disorder along the c direction, apparently due to random stacking faults of the a–b sheets along the c-axis ($c = 1.313$ nm). This is especially visible as substantial diffuse scattering intensities for reflections with large Bragg indices l.

Magnetic susceptibility measurements with the magnetic field aligned within the a–b plane displayed in Fig. 1 indicate the onset of the diamagnetic signal at 38 K. The width of transition (10–90% criterion) amounts to about 3.5 K. As is clearly seen in the zero-field cooled (ZFC) signal, the diamagnetic signal does not level off but continues to decrease to lowest temperatures indicating some inhomogeneities in the crystals.

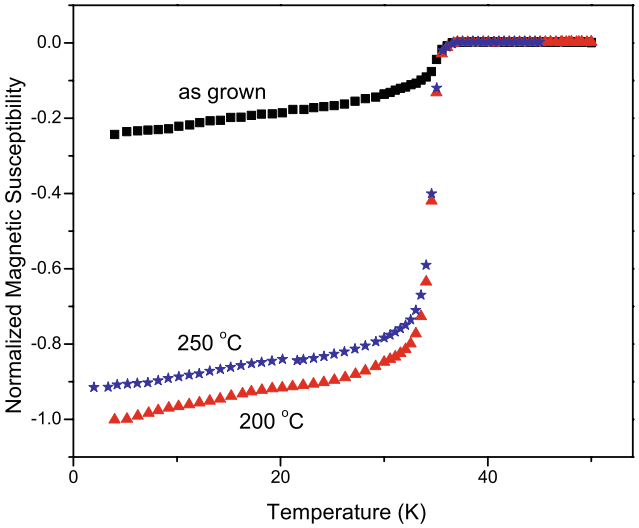

Fig. 2 (Color online) Temperature dependence of the magnetization measured at a field of 10 Oe after the sample had been cooled in zero-field for an as-grown crystal and the identical crystal after annealing at 200 °C and 250 °C

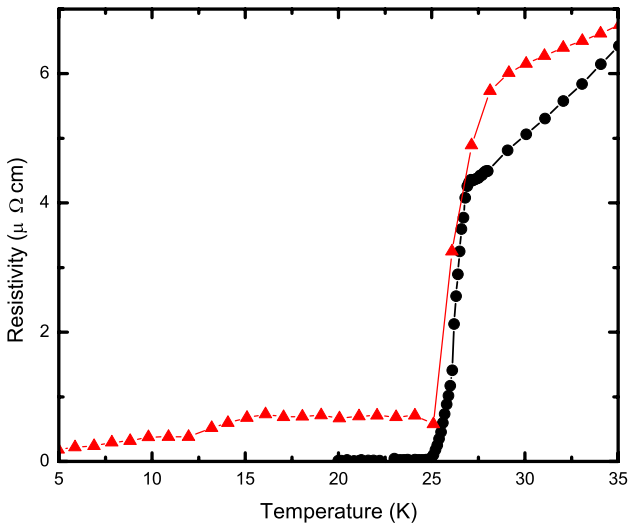

Fig. 3 (Color online) Temperature dependence of the electrical resistivity for two samples from the same batch of $Ba_{25}K_{75}Fe_2As_2$

Inhomogeneities and the continuous decrease of the diamagnetic signal at low temperatures can be significantly reduced by annealing the crystals at moderate temperatures. For this purpose, a crystal was sealed in an evacuated quartz glass tube under He exchange gas (∼0.3 bar) in the tube, and after the magnetization had initially been measured, the quartz glass tube with the crystal was placed into a furnace and kept at a fixed temperature for 5 hours. After rapid quenching the magnetization of the crystal was measured again. This procedure was repeated several times with successively increasing the annealing temperature. After annealing at 200 °C the diamagnetic flux exclusion increased by a factor of ∼5 indicating increased homogeneity of the Ba/K distribution leading to a reduction of strain effects. Annealing at 250 °C and temperatures above, however, was found to reduce the diamagnetic signal (cf. Fig. 2). This result is assigned to a loss of K and a gradual change of stoichiometry in the crystals. To examine stoichiometry and Ba/K ordering effects we grew single crystals aiming at a higher concentration of K, namely $Ba_{25}K_{75}Fe_2As_2$. Several crystals from this batch were examined by measuring their resistivity and magnetization as a function of temperature. All samples exhibit an onset of the diamagnetic signal at about 27 K. Some crystals however, showed a subsequent sharp step-shape reduction of the magnetization at about 15 K indicating a second superconducting phase within the crystals with a T_C near 15 K. An example of the resistivity results obtained on two crystals with composition $Ba_{0.25}K_{0.75}Fe_2As_2$ is shown in Fig. 3.

Using SEM and electron probe microanalysis, we examined in more detail the elemental composition of one of the crystals which showed the second superconducting transition with a $T_C \approx 15$ K. The SEM picture of the sample clearly reveals a sharp line separating crystallites with significantly different elemental composition of Ba and K (see Fig. 4(b)). The results of a microanalyzer scan along a line of ≈200 μm length across the transition on the crystal's surface (thick line shown in the SEM picture) is displayed in Fig. 4(b). While the As and Fe content along the scan is relatively constant, a simultaneous sharp drop in the K and a sharp increase of Ba content becomes evident at the phase boundary. While in the darker region the elemental composition of the sample corresponds rather well to $Ba_{0.35}K_{0.65}Fe_2As_2$ (lower left part of the crystal in Fig. 4(a)), the composition in the brighter areas (upper right-hand part of the crystal in Fig. 4(a)) indicates a composition $Ba_{0.7}K_{0.3}Fe_2As_2$, however with a rather large variation of the K and Fe content along the scanned line as shown in Fig. 4(b). This compositional scatter may be the reason why in the superconducting phase below T_C the resistivity of this crystal does not vanish (cf. Fig. 3). The sharpness of the phase boundary separating the two parts of the crystal with different elemental compositions possibly indicates that KFe_2As_2 and $BaFe_2As_2$ have a miscibility gap and that rather rational phase boundaries are assumed. This implies the question of whether or not K atoms randomly substitute Ba atoms or whether intact K and Ba layers survive which stack in the appropriate ratios. However, our preliminary x-ray results indicate random distribution of K for Ba since no extra reflections from superlattice formation due to ordering of K and Ba layers were observed. In any case, as a remarkable observation, the established route of crystal growth at non-constant temperature can lead to crystals with substantial compositional gradients or even inter-growth of crystals with largely different compositions. We finally discuss the issue of possible Sn substitution and its influence

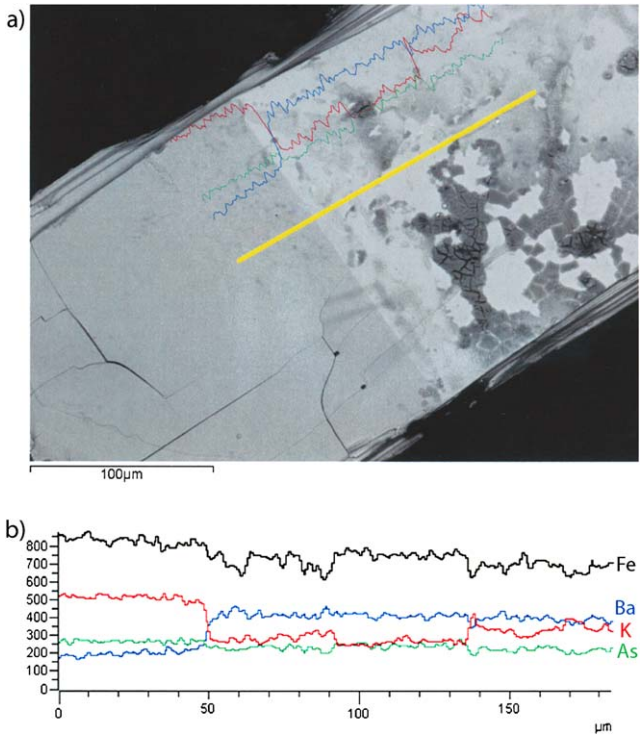

Fig. 4 (Color online) SEM image as well as a the result (*traces* in lower part of the figure) of a microprobe analysis scanned along a ≈200 µm traces of the crystal indicated by the solid (*yellow*) bar on the crystal. The crystal was grown in an Sn flux aiming at a composition $Ba_{0.25}K_{0.75}Fe_2As_2$. The *speckled dark areas* seen on the right-hand part of the crystal are due to the adhesive used for holding the sample during resistivity measurement

on the superconducting properties. We studied a total of 5 crystals showing very similar characteristics in their superconducting properties as the crystal described in detail above. These investigations gave no indication that Sn impurities in quantitative amounts are present that could play a decisive role for the variation of the superconducting properties of these compounds. We conclude that the variation of the K and Ba content, and possibly the stacking and the ratio of non-substituted intact Ba and K layers throughout the crystal are the most important factor in determining the electronic and magnetic properties. A careful examination of crystal growth conditions and the microscopic distribution of Ba and K atoms appears to be necessary to optimize the superconducting properties of these phases.

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